Stability of Biodiesel from Non Edible Oils

J. Madarasz[1,] Amit Kumar[2]
[1] Department of Inorganic and Analytical Chemistry
Budapest University of Technology and Economics
[2] Department of Mechanical Engineering, university of Alberta, Edmonton
Alberta, Canada
[1]jmadarasz.hungary@gmail.com, [2]amit.kumar@ualberta.ca

***Abstract*-Alternate fuels are being explored world over due to increasing environmental concern and diminishing petroleum reserves. In South Asian countries like India, Pakistan, Sri Lanka etc, biodiesel can be harvested and sourced from non-edible seed oils like Jatropha. In fact, implementation of biodiesel from Jatropha in India will lead to many advantages like providing green cover to wasteland, support to agricultural and rural economy, and reduction in dependency on imported crude oil and reduction in air pollution. Although biodiesel is environmentally compatible, it is susceptible to oxidation. The research on biodiesel stability has been put on top priority. Biodiesel from Jatropha curcas oil is relatively unstable on storage and forms residual products such as insoluble gums and aldehydes that may cause engine problems like filter clogging, injector coking, and corrosion of metal parts. The present paper deals with the the review of work done for stability of biodiesel from Jatropha curcas oil all over the world.**

Keywords-biodiesel; oxidation stability; thermal stability; induction period

I. INTRODUCTION

In recent years, the biodiesel, as an eco-friendly and renewable fuel substitute for diesel has been getting the interest of scientists and workers all over the world. The research conducted so far have revealed the suitability of B_{20} blends as no engine modification is required and the energy contents and output power level are similar to that obtained from petro- diesel. In developing countries like India, biofuel program of Government of India has been launched where apart from fuel; alcohol production from sugar/starch based feedstock, the Jatropha curcas plant has been planted on massive scale on waste/ degraded or other lands to open new avenues for producing biodiesel from Jatropha curcas oil thereby reducing/saving foreign exchange needed to import the petroleum fuel. In biodiesel production, India is on 8^{th} position with 0.03 billion liters of biodiesel production per year [1, 2 and 3].

Further, increased environmental degradation owing to fast depleting petroleum reserves and strong agro-based economy of the country are promoting the use of biodiesel as an alternate renewable transport fuel. In USA and Europe, biodiesel derived from vegetable oil and animal fats is already been used to reduce air pollution to improve fuel supply situation and to reduce dependence on fossil fuel, which are limited and localized to specific regions.

In different countries of the world, different resources are used for biodiesel production. For example, USA and Europe, the surplus edible oils like soybean oil, sunflower oil and rapeseed oil are being used as feedstocks for the production of biodiesel. Since India is net importer of edible vegetable oils, these oils are therefore not available for conversion to biodiesel. India has the potential of becoming the world's leading producer of biodiesel, as it can be ''harvested,'' and produced from non-edible oils like *Jatropha Curcas, Pongamia Pinnata, Madhuca Indica* plants etc. As indicated above, India is focusing on *Jatropha Curcas* plant, which can grow in arid, semiarid and wasteland, requires little water and fertilizer, can survive on infertile soils and not browsed by the cattles. Further, it is resistant to pests and has high seed production for 30–40 years or more with 30- 40% oil contents. Developing courtiers like India has about 80–100 million hectares of wasteland, that can be used for the Jatropha cultivation. The increasing use of biodiesel in India will provide green cover to wasteland, support the agricultural and rural economy, reduce the dependency on imported crude oil and improve the environmental emissions [4].

Even though, 12 *Jatropha* species are reported by several Indian floras, research has been confined to nine species only. Among all the *Jatropha* species, *J. curcas* is the most primitive form and has the potential for biodiesel and for medicinal purposes [5]. Table 1 gives the morphological and other features of all the 12 *Jatropha* species.

In almost all the biodiesels, significant amounts of esters of oleic, linoleic or linolenic acids are present and the trend of increasing stability was linolenic < linoleic < oleic [6]. These esters undergo auto-oxidation with different rates depending upon the number and position of the double bonds and results in formation of a series of by-products, like acids, esters, aldehydes, ketones, lactones, etc. which renders the use of biodiesel as fuel due to problems experienced during engine operation like fuel filter clogging, fuel atomization etc. the presence of above byproducts of auto-oxidation and other reactions affect the biodiesel quality and hence make it unstable and unfit for use in engines. The basic aim of the paper is to review the work done by different researchers in field of stability of biodiesel from Jatropha curcas oil all over the world.

II. MECHANISM OF FUEL STABILITY

Fatty acid chain/ biodiesel with unsaturation in its fatty acids offers high reactivity with O_2, especially, when it is placed in contact with air/ water. As the Jatropha curcas biodiesel contains about 75% of unsaturated fatty esters, its oxidation stability is expected to be seriously impacted. Further, the fatty oils with more poly unsaturation, are more prone to oxidation [7- 34]. Literature reveals the relative rate of oxidation for the methyl esters of oleic (18:1), linoleic (18:2), and linolenic (18:3) acids to be 1:12:25 respectively [21]. Further work has indicated that the rate of oxidation of pure unsaturated fatty acids as measured by oxygen

consumption in closed system is proportional to the number of bis-allylic carbons present[20, 22]. As the linoleic (18:2) and linolenic (18:3) acid content in fatty oils or esters increases, the oxidation stability decreases and as fatty oils or the alkyl monoesters of fatty oils are oxidized, the hydroperoxide (ROOH) levels also increased indicating the drop in the quality of the oil or esters. [23].

TableI MORPHOLOGICAL FEATURES AND TRAITS OF DIFFERENT SPECIES OF JATROPHA [5]

Species	**Native place**	**Oil (%) Content**	**Propagation methods**
Jatropha curcas	Tropical America	30–42	Seed, cutting, grafting, air layering and tissue culture
Jatropha gossypifolia	Brazil	28–30	Seed and cuttings
Jatropha glandulifera	India	20–27	Seed and cuttings
Jatropha multifida	South America	32–40	Seed and by cuttings during spring
Jatropha tanjorensis	India	Sterile	Cuttings
Jatropha podagrica	Panama	Up to 54	Seed and by division of branches
Jatropha integerrima	West Indies	No report available	Cuttings
Jatropha pandurifolia	Cuba	No report available	Seed and cuttings
Jatropha villosa	India	No report available	No report
Jatropha nana	India	No report available	Seed
Jatropha heynei	India	No report available	Seed
Jatropha maheswari	India	No report available	No report

example, biodiesel from sunflower oil (BDSU) with only 21.1% saturates, gave a induction period of 3.23 h while the palm oil biodiesel (BDP) with 43.4% saturates exhibited induction period of 13.37 h indicating good stability. The reason for good stability of palm oil biodiesel is due to the resistance to auto-oxidation of saturated fatty acids. Palm oil has maximum proportion of saturates making it less susceptible towards oxidation as compared to JCB.

At sufficiently high temperatures, the methylene-interrupted polyunsaturated olefin structure begins to isomerize to more stable conjugated structure. Once this isomerization has begun, a conjugated diene group from one fatty acid chain can react with a single olefin group from another fatty acid chain to form a cyclohexene ring [18, 36, and 37]. This reaction between a conjugated di-olefin and a mono-olefin group, called the Diels Alder reaction, and becomes important at temperatures of 250-300°C or more. The reaction results in the formation of carbonyl compound such as aldehyde (formed from hydroperoxides) or high molecular weight polymers (formed from peroxide radicals) which increases the viscosity of biodiesel.

Literature has further revealed that very little work has been reported on thermal stability of JCB. However, some authors have studied the thermal behavior of Jatropha curcas biodiesel using TGA/DTA analysis. TG/DTG and PDSC experiments were used to obtain information on the temperature-controlled combustion of the biofuels synthesized. TG/DTG curves were obtained using a simultaneous analyzer SDT 2960 (TA Instruments), alumina pans, under dry air atmosphere (100 mL min-1), heating rate of 10^0C/ min and temperature range from 10^0 to 700^0C [38]. The equipment was calibrated by the TG mass (using standards masses and empty beam), DTA baseline and temperature adjust (evaluation of melting endotherms of pure zinc, tin and indium metals) [39]. The TG/DTG curves of physic nut oil (Fig. 1) show three peaks of thermal decomposition that were assigned to the volatilization and/or combustion of triacylglycerides. The TG/DTG curves of biodiesel (Fig. 2) show only two mass loss steps indicating volatilization and/or combustion of ethyl esters (the first step), mainly, the ethyl oleate and linoleate, once oleic and linoleic fatty acids are the most abundant components of the initial oils. Such results are in agreement with the literature where two mass loss steps for biodiesel were observed [40].

The oxidation stability tests were carried out at 100 °C and 120 °C by Sarin et al. [35]. As anticipated, the oxidation process was accelerated with increase in temperature. However, no difference in relative stability was noticed and biodiesel from the oil having large fraction of saturated fatty acids like palm was found to be still better than biodiesel from other oil sources like Jatropha with larger fraction of unsaturated fatty acids.

The customer acceptance, standardization and quality assurance are the key factors for introducing new alternatives of liquid biofuels as biodiesel and its blends into the market and storage stability is one such criteria. The storage stability problem of biodiesel during storage is expected to be more severe than for commercial diesel fuel. The resistance of biodiesel to oxidative degradation during storage is, therefore, an important increasingly important issue for the viability and sustainability of alternative fuels.

Stability may be affected by interaction with contaminants, light, factors causing sediment formation, which bring about changes in the color and hence reduce the clarity of the fuel [25, 26, 41]. Several authors have performed the long term storage test on biodiesel stability and studied the effect of

physical properties of the fuel with respect to time [27-30, 36-38] and it was reported that viscosity, peroxide value, acid value and density of biodiesel increases when stored for two years while the heat of combustion decreases [27-31].

Sarin et al. [42] have studied the influence of metal contaminants on the oxidation stability of Jatropha ME with particular reference to the presence of transition elements likely to be present in the metals of which the storage tanks and barrels are made. The transition metals like iron, nickel, manganese, cobalt, and copper commonly found in metal containers were blended with varying concentrations (ppm) in JCB samples. Metals were weighed using digital

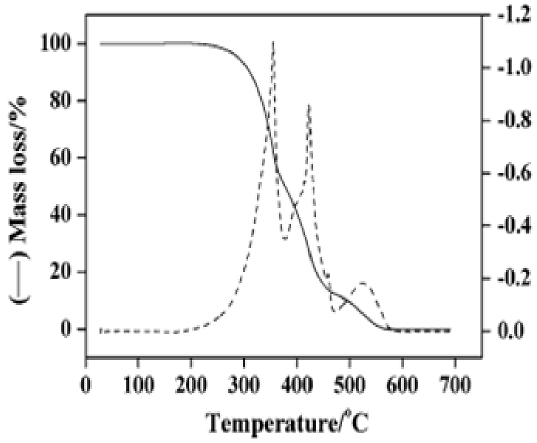

Fig. 1 TG/DTG Curves of from different crops of physic nut oil in air atmosphere

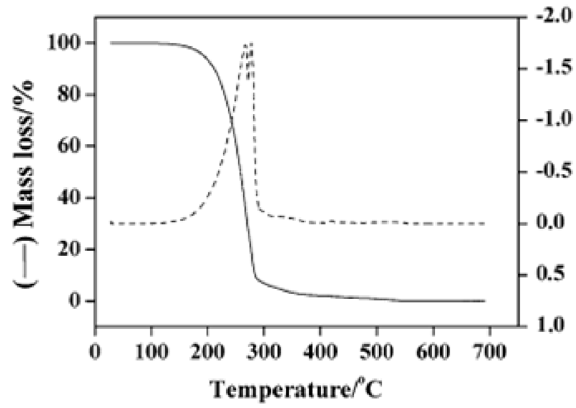

Fig. 2 TG/DTG Curves of from different crops of physic nut biodiesel oil in air atmosphere

weighting machine. The presence of these metals was found to depress the oxidation stability of biodiesel, as measured by the IP (fig. 3) due to the acceleration of free radical oxidation and metal-mediated initiation reaction which shows that copper had strongest catalytic effect and other metals like iron, nickel, manganese, and cobalt also had strong negative influence on the oxidation stability. The fig also shows that for all the metallic contaminants, IP values became almost constant as the concentration of metal is increased. This proves that the influence of metals was catalytic, as even small concentrations of metals had nearly the same effect on the oxidation stability as the higher metal concentration has. The dependence of the oxidation stability on the type of metal confirms that Rancimat is suitable laboratories test that to correlate long-term stability.

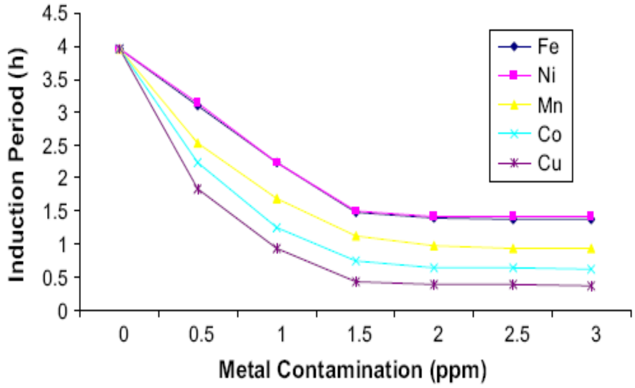

Fig. 3 Influence of metal contamination on oxidation stability

However, the effect of other storage parameters, e.g., exposure to atmosphere, environment temperature, cold storage, type of container etc on stability of JCB has not yet been reported in the literature.

III. METHODS TO INCREASE THE STABILITY

Oxidation can be significantly slowed down by the use of antioxidants, the chemicals which inhibit the oxidation process. Two types of antioxidants are generally known: natural and synthetic [43]. The mechanism of all antioxidants is shown below in fig.4.

$$ROO^{\cdot} + AH \rightarrow ROOH + A^{\cdot}$$

$$A^{\cdot} \rightarrow \text{stable product}$$

Fig.4 Mechanism of antioxidants

The effectiveness of antioxidant is generally measured by stressing a fatty oil or ester molecule both with and without the antioxidant [35- 76].

A. Natural Antioxidants

Tocopherol is a phenolic compound that exists in four isomers (α, β, γ, δ), all of which occur naturally in vegetable oils [44]. Depending on fatty oil processing conditions, tocopherols may be retained, partially lost, or completely lost [45, 46]. Similarly, post-transesterification processing of biodiesel like distillation can remove any tocopherols that were originally present in the vegetable oil feed.

B. Synthetic Antioxidants

These antioxidants are added in oils or biodiesel to increase its stability. Some of the most common synthetic antioxidants are given in table2:

TableII DIFFERENT SYNTHETIC ANTIOXIDANTS WITH THEIR CHEMICAL FORMULAE

Name of antioxidant	Main features
Pyrogallol(PY)	M.P. = 131-134 °C B.P. = 309°C Density = 1.45 g/cm^3 Molar mass = 126.11 g/mol
Gallic Acid(GA)	M.P. = 250 °C Density = 1.7 g/cm^3 (anhydrous) Molar mass = 170.12 g/mol
Propyl Gallate(PG)	M.P. = 150 °C B.P. = Decomposes Molar mass = 212.20 g/mol
Catechol(C)	M.P. = 105 °C B.P. = 245.5°C Density = 1.344 g/cm³, solid Molar mass = 110.1 g/mol
Nordihydroguaiaretic acid(NDGA)	Molar mass = 302.36 g/mol

Different synthetic antioxidants had different effects on the stability of biodiesel, depending on the feedstocks without affecting the properties such as viscosity, cold filter plugging point (CFPP), density, carbon residue and sulfated ash except acid value that appears to be affected slightly by the addition of antioxidants [77, 78].

Sarin et al. [35] have worked on blending Jatropha biodiesel with Palm biodiesel and found that Jatropha biodiesel when blended with palm biodiesel results in mixture that has efficient and improved low temperature property as well as good oxidation stability. The reason of blending is that Jatropha biodiesel has poor oxidation stability with good low temperature properties while Palm biodiesel has good oxidative stability but poor low temperature properties. The combinations of Jatropha and Palm biodiesel give an additive effect on these two critical properties of biodiesel.

The stability of biodiesel, being a critical quality parameter, requires the addition of antioxidants to ensure improved fuel quality at all points along the distribution chain. To meet EN 14112 specification, antioxidants concentration of about 200 ppm required for biodiesel which is much higher than that required for palm biodiesel as shown in fig. 5. In order to minimize the dosage of antioxidant, appropriate blends of Jatropha and palm biodiesel were prepared. It was found that the antioxidant dosage could be reduced by 80–90%, if Palm oil biodiesel is blended with Jatropha biodiesel at around 20–40% concentration.

It may be noted that of five metals investigated, copper has the strongest detrimental and catalytic effect compared to other metallic elements. The dependency of the oxidation stability on the type of metals showed that long-term storage tests using different types of metallic containers to examine the influence of container material on oxidation stability of biodiesel, may be replaced by the significantly faster Rancimat test serving as an accelerated storage test. The oxidation stability of metal contaminated JBD has been found to increase with increase in dosage of phenolic 2,6-ditertiarybutyl hydroxytoluene antioxidant (AO-1) as shown in fig.6.

As reported elsewhere, the formation of oxidation products in biodiesel impacts the fuel quality of biodiesel when exposed to a number of environmental factors, as a results, causes various operational problems during engine operation.

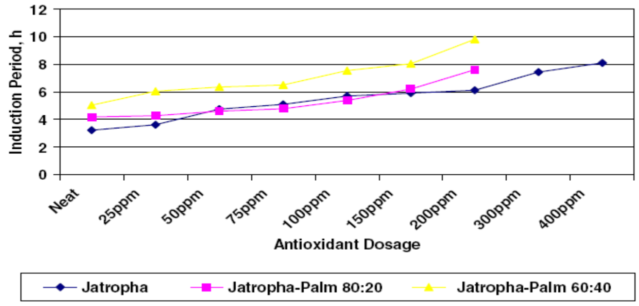

Fig.5 Antioxidant dose optimization for jatropha and palm biodiesel

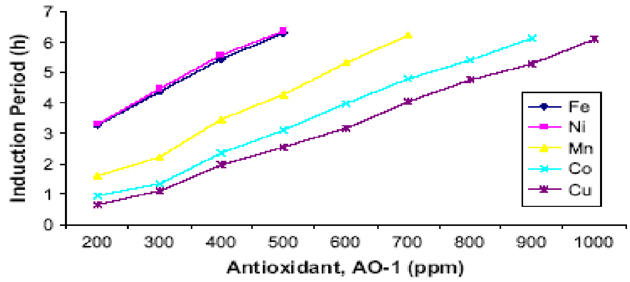

Fig.6 Influence of antioxidant concentration on the oxidation stability of metal contaminated (2 ppm) jatropha methyl ester

A number of research papers have reported the work on storage, thermal and oxidation stability of biodiesel from edible oils but very little work is reported on the stability of biodiesel from non-edible oil resources like Jatropha curcas, pongamia, etc. [39, 41, 67]. The maintenance of biodiesel fuel quality depends on the development of technologies to increase its resistance to oxidation during long-term storage.

Looking at high consumption of edible oils in developing countries the indigenous production is not coping with the consumption and hence significant amount is imported. And there is no possibility of diverting edible oils for biodiesel production. The non-edible oil resources, on the other hand, may be used for this purpose. *Mathuca indica*, *Shorea robusta*, *Pongamia globra*, *Mesua*, *Mallotus philillines*, *Garcinea indica*, *Jatropha curcas* and *Salvadova* have been identified as non- edible oil resources.out of which jatropha curcas is being given top priority for its planmtation by Gov of India under national biodiesel program using waste/ semiarid land. As per an estimate, the potential availability of non-edible oil in India is about 1Million ton/yr.

In view of possibility of Jatropha curcas plant is being viewed as future source of biodiesel in the country and therefore, the maintenance of its fuel quality similar to petro-diesel becomes the need of the hour. Considerable efforts have therefore been directed to improve the oxidation, thermal and storage stability of JCB only so that the fuel quality of new fuel substitute of diesel can be ensured and indigenous fuel quality specifications can be developed.

IV. CONCLUSIONS

In South Asian countries like India, Pakistan, Sri Lanka etc, biodiesel can be harvested and sourced from non-edible seed oils like Jatropha. In fact, implementation of biodiesel from

Jatropha in India will lead to many advantages like providing green cover to wasteland, support to agricultural and rural economy, and reduction in dependency on imported crude oil and reduction in air pollution. In the recent years, the production of biodiesel from non- edible oil resources, improvement in the quality of biodiesel from the print of its acceptability by the markets and consumers has been accorded top priority by the scientific community all over the world. The biodiesel quality is affected by large number of parameters which can be categorized by oxidation, thermal and storage stability parameters. Considerable literature is available on the above stabilities of biodiesel from edible oils but very few work is available on the stability of biodiesel from non-edible oil resources like Jatropha curcas, pongamia, etc. which has prompted us to carryout stability studies on Jatropha curcas biodiesel only as it is becoming future transport fuel in the developing. In the present paper the oxidation, storage and thermal stability studies and use of antioxidants to improve the fuel quality has also been discussed.

REFERENCES

[1] S. Jain, M.P. Sharma. Prospects of biodiesel from Jatropha in India: A review. Renewable and Sustainable Energy Review 2010; 14(2): 763-771.

[2] The energy data directory year book (TEDDY), 2009 published by The energy Research Institute (TERI), New Delhi, India.

[3] Renewables.2007.Global Status Report. http://www.ren21.net/Rdf/RE2007_Global_Status_Report.pdf

[4] S. Jain, M.P. Sharma. Biodiesel production from Jatropha curcas oil. Renewable and Sustainable Energy Reviews (2010), doi:10.1016/j.rser.2010.07.047

[5] P.R. Krishnan, M. Paramathma. Potentials and *Jatropha* species wealth of India. Current Science 2009; 97(7): 1000-1004.

[6] K. Miyashita, T. Takagi. Study of the oxidative rate and prooxidant activity of free fatty acids. Journal of the American Oil Chemists Society 1986;63(10): 1380–4.

[7] B.K. Barnwal,M.P. Sharma. Prospects of biodiesel production from vegetable oils in India. Renewable and Sustainable Energy Reviews 2005; 9: 363–78.

[8] M.P. Sharma, R. Agarwal. Non-edible oils as potential resources of biodiesel. In Proceedings of the 23rd National Convention of Chemical Engineers on Recent Trends in Chemical Engineering held at chemical engineering department, IIT Roorkee, Roorkee, India; 2007. p. 202–11.

[9] S. Jain, M.P. Sharma, Evaluation of Engine Performance on Biodiesel from Waste Cooking Oil. Presentated at the 4th international conference on "Energy Informatics and Cybernetics (EIC-2008)" held at Orlando, Florida, USA on June 29- July 02, 2008.

[10] A. Monyem, J.H. Van Gerpen. The effect of biodiesel oxidation on engine performance and emissions. Biomass & Bioenergy 2001; 20: 317–25.

[11] A. Monyem, J.H. Van Gerpen, M. Canakci. The effect of timing and oxidation emissions from biodiesel-fueled engines. Transactions of the ASAE 2001; 44: 35–42.

[12] F. Roseli Ap, Vanessa da Silva Oliveira, Scabio Ardalla. Oxidative stability of biodiesel from soybean oil fatty acid ethyl esters. Scientia Agricola (Piracicaba Brazil) 2005; 62(3): 291–5.

[13] S. Jain, M.P. Sharma. Kinetics of acid base catalyzed transesterification of Jatropha curcas oil. Bioresource Technology 2010; 101 (20): 7701-7706.

[14] G. Knothe, R.O. Dunn. Dependence of oil stability index of fatty compounds on their structure and concentration and presence of metals. Journal of the American Oil Chemists Society 2003; 80: 1021–6.

[15] J.H. Van Gerpen, Hammond EG, Liangping Y, Monyem A. Determining the influence of contaminants on biodiesel properties. SAE paper 971685; 1997.

[16] K. Yamane, K. Kawasaki, K. Sone, T. Hara, T. Prakoso. oxidation stability of biodiesel and its effect on diesel combustion and emission characteristics. International Journal of Engine Research 2007; 8(3): 307–19.

[17] R.O. Dunn. Effect of temperature on the oil stability index (OSI) of biodiesel. Energy & Fuels 2008; 22(1): 657–62.

[18] M.W. Formo, Jungermann E, Noris F, Sonntag NOV. Bailey's industrial oil and fat products. 4th edition John Wiley and Son 1979; 1(4): 698–711.

[19] J.C. Cowan. Encyclopedia of chemical technology, Wiley Interscience; 1979; 8(3): 130–50.

[20] D.F. Church, W.A. Pryor. Free-radical chemistry of cigarette smoke and its toxicological implications. Environmental Health Perspectives 1985; 64: 111–26.

[21] F.D. Gunstone, T.P.J. Hilditch. Triglyceride composition of tobacco seed oil. Journal of the American Oil Chemists Society 1945; 836.

[22] G. Knothe. Structure indices in fatty acid chemistry how relevant is the iodine value? Journal of the American Oil Chemists Society 2002; 79(9): 847–54.

[23] W.E. Neff, T.L. Mounts, W.M. Rinsch, H. Konishi. Journal of the American Oil Chemists Society 1993; 70(2): 163–8.

[24] A.A. Refaat. Correlation between the chemical structure of biodiesel and its physical properties. International Journal of Environmental Science and Technology 2009; 6(18): 677–94.

[25] M. Canakci, A. Monyem, J. H. Van Gerpen. Accelerated oxidation processes in biodiesel. Transaction of the ASAE 1999; 42: 1565–72.

[26] M. Mittelbach, S. Gangl. Long storage stability of biodiesel made from rapeseed and used frying oil. Journal of the American Oil Chemists Society 2001; 78(6): 573–7.

[27] P. Bondioli, A. Gasparoli, L.D. Bella, S. Tagliabue. Evaluation of biodiesel storage stability using reference methods. European Journal of Lipid Science & Technology 2002; 104: 777–84.

[28] P. Bondioli, A. Gasparoli, L.D. Bella, S. Taghliabue, G. Toso. Biodiesel stability under commercial storage conditions over one year. European Journal of Lipid Science & Technology 2003; 105: 735–41.

[29] P. Bondioli, A. Gasparoli, A. Lanzani, E. Fedeli, S. Veronese, M. Sala. Storage stability of biodiesel. Journal of the American Oil Chemists Society 1995; 72(6): 699–702.

[30] Monyem, M. Canakci, J.H. Van Gerpen. Investigation of biodiesel thermal stability under simulated in-use conditions. Applied Engineering in Agriculture 2000; 16(4): 373–8.

[31] Miyata, Y. Takei, K. Tsurutani, M. Okada. Effects of bio-fuels on vehicle performance: degradation mechanism analysis of bio-fuels. SAE paper 2004-01-3031; 2004.

[32] K. Andersson, H. Lingnert. Influence of oxygen and copper concentration on lipid oxidation in rapeseed oil. Journal of the American Oil Chemists Society 1998; 75(8): 1041–6.

[33] W.E. Neff, M.A. El-Agaimy, T.L. Mounts. Oxidative stability of blends and interesterified blends of soybean oil and palm olein. Journal of the American Oil Chemists Society 1994; 71(10): 1111–6.

[34] L.M. DuPlessis, J.B.M. DeVilliers, W.H. Van der Walt. Stability studies on methyl and ethyl fatty acid esters of sunflowerseed oil. Journal of the American Oil Chemists Society 1985; 62(4): 748–52.

[35] R. Sarin, M. Sharma, S. Sinharay, R.K. Malhotra. Jatropha–palm biodiesel blends: an optimum mix for Asia. Fuel 2007; 86(10–11): 1365–71.

[36] N.T. Joyner, J.E. McIntyre. The oven test as an index of keeping quality. Oil and Soap 1938; 15: 184–6.

[37] Determination of biodiesel oxidation and thermal stability: final report. Prepared by System Lab Services Division of Williams Pipe Line Company; February 1997.

[38] M.V. Ko¨k, C. Acar. Kinetics of crude oil combustion. J Therm Anal Calorim. 2006; 83(2): 445–9.

[39] M.V. Ko¨k, G. Pokol, C. Keskin, J. Madara´sz, S. Bagci. Light crude oil combustion in the presence of limestone matrix. Journal of Thermal Analysis and Calorimetry 2004; 75: 781–6.

[40] M.B. Dantas, M.M. Conceic¸a˜o, V.J. Jr. Fernandes, N.A. Santos, R. Rosenhaim, A.L.B. Marques, et al. Thermal and kinetic study of corn biodiesel and obtained by the methanol and ethanol. Journal of Thermal Analysis and Calorimetry 2007; 87(3): 835–9.

[41] S. Jain, M.P. Sharma. Stability of biodiesel and its blends: A review. Renewable and Sustainable Energy Review 2010; 14(2): 667- 678.

[42] A. Sarin, R. Arora, N.P. Singh, M. Sharma, R.K. Malhotra. Influence of metal contaminants on oxidation stability of Jatropha biodiesel. Energy 2009; 34(9): 1271- 1275.

[43] F. Gugumus, J. Pospisil, P.P. Klemchuk. Oxidation inhibition in organic materials. CRC Press; 1990; 2: 29- 163.

[44] A. Kamal-Eldin, A. Lars-Ake. The chemistry and antioxidant properties of tocopherols and tocotrienols. Lipids 1996; 31(7): 671–701.

[45] E.R. Sherwin, B.M. Luckadoo. Effect of stabilization crude whale oil. Journal of the American Oil Chemists Society 1970; 47: 19–23.

[46] M.H. Chanine, R.F. Mac Neill. Effect of selected antioxidants on stability of virgin olive oil. Journal of the American Oil Chemists Society 1974; 51: 37–41.

[47] M.Y. Yung, D.B.J. Min. Food quality and preference. Journal of food science 1990;55:1464–5.

[48] Y.C. Liang, C.Y. May, Foon Cheng Sit, Ngan Ma Ah, Hock Chuah Cheng, Yusof Basiron. The effect of natural and synthetic antioxidants on the oxidative stability of palm diesel. Fuel 2006; 85: 867–70.

[49] M.A. Augustin, S.K. Berry. Effectiveness of antioxidants in refined, bleached and deodorized palm olein. Journal of the American Oil Chemists Society 1983; 60.

[50] C.W. Fritsch, V.E. Weiss, R.H. Anderson. Effect of antioxidants on refined palm oil. Journal of the American Oil Chemists Society 1975; 52(12): 517- 519.

[51] E. Sendzikiene, V. Makareviciene, P. Janulis. Oxidation stability of biodiesel fuel produced from fatty wastes. Polish Journal of Environmental Studies 2005; 14(3): 335–9.

[52] J. Xin, H. Imahara, S. Saka. Kinetics on the oxidation of biodiesel stabilized with antioxidant. Fuel 2009; 88(2): 282–6.

[53] M.E. Gordon, E. Mursi. A comparison of oil stability based on the Metrohm Rancimat with storage at 20^0C. Journal of the American Oil Chemists Society 1994; 71: 649–51.

[54] T. Asa, M.A. Augustin. Effect of TBHQ on quality characteristics of RBD olein during frying. Journal of the American Oil Chemists Society 1986; 63(9): 1169– 72.

[55] [55] R. Dinkov, G. Hristov, D. Stratiev, A.V. Boynova. Effect of commercially available antioxidants over biodiesel/diesel blends stability. Fuel 2009; 88(4): 732–7.

[56] [56] R. Becker, A. Knorr. An evaluation of antioxidants for vegetable oils at elevated temperatures. Lubrication Science 1996; 8–2: 95–117.

[57] C.W. Everson, G.J. Miller, F.W. Quackenbush. Comparison of antioxidants for fats on an equivalent molar basis. Journal of the American Oil Chemists Society 1957; 34: 81–3.

[58] E.R. Sherwin, J.W. Thompson. Tert-Butylhydroquinone. An antioxidant for fats and oils and fat-containing foods. Food Technology 1967; 21: 106–10.

[59] R. Sarinh, M. Sharma, S. Sinharay, R.K. Malhotra. Jatropha–palm biodiesel blends: an optimum mix for Asia. Fuel 2007; 86(10–11): 1365–71.

[60] I. Hiroaki, M. Eiji, H. Shusaku, S. Saka. Thermal stability of biodiesel in supercritical methanol. Fuel 2008; 87(1): 1–6.

[61] H. Prankl, H. Schindlbauer. Oxidation stability of fatty acid methyl esters. In: 10th European conference on biomass for energy and industry; 1998.

[62] H.A. Abou-Gharbia, A.A.Y. Shehat, F. Shahidi. Effect of processing on oxidative stability and lipid classes of sesame oil. Food Research International 2000; 33(5): 331–40.

[63] G. Yildiz, R.L. Wehling, S.L. Cuppett. Comparison of four analytical methods for the determination of peroxide value in oxidized soybean oils. Journal of the American Oil Chemists Society 2003; 80(2): 103- 107.

[64] S. Kazutaka, T. Prakoso, K. Kiyoshi, Y. Koji. A study on oxidation stability of biodiesel fuel. Nippon Kikai Gakkai Kansai Shibu Teiji Sokai Koenkai Koen Ronbunsh 2005; 80: 337–8.

[65] K. Nakamura, S. Saka, M. Ikegami. Research for oxidation stability of biodiesel fuel and its improvement of the fuel quality. Energy and Resources 2006; 27: 426–30.

[66] C.Y. Lin, H.A. Lin, L.B. Hung. Fuel structure and properties of biodiesel produced by the peroxidation process. Fuel 2006; 85(12– 13): 1743–9.

[67] B.R. Moser, Sharma BK, Doll KM, Erhan SZ. Diesters from oleic acid: synthesis, low temperature properties, and oxidation stability. Journal of the American Oil Chemists Society 2007; 84: 675–80.

[68] J. Xin, H. Imahara, S. Saka. Oxidation stability of biodiesel fuel as prepared by supercritical methanol. Fuel 2008; 87(10–11): 1807–13.

[69] G. El Diwani, S. El Rafie. Modification of thermal and oxidative properties of biodiesel produced from vegetable oils. International Journal of Environmental Science and Technology 2008; 5(3): 391–400.

[70] J.Y. Park, D.K. Kim, J.P. Lee, S.C. Park, Y.J. Kim, J.S. Lee. Blending effects of biodiesels on oxidation stability and low temperature flow properties. Bioresource Technology 2008; 99(5): 1196–203.

[71] H. Tang, G.R.C. De, S.O. Salley, K.Y. Ng Simon. The oxidative stability of biodiesel: effects of FAME composition and antioxidant. Lipid Technology 2008; 20(11): 249–52.

[72] H. Tang, A. Wang, S. Salley, et al. The effect of natural and synthetic antioxidants on the oxidative stability of biodiesel. Journal of the American Oil Chemists Society 2008; 85(4): 373–82.

[73] L.M. Das, D.K. Bora, S. Pradhan, M.K. Naik, S.N. Naik. Long-term storage stability of biodiesel produced from Karanja oil. Fuel 2009; 88 (11): 2315- 2318.

[74] E.O. Aluyor, K.O. Obahiagbon, M. Ori-jesu. Biodegradation of vegetable oils: a review. Scientific Research and Easy 2009; 4(6): 543–8.

[75] B.K. Sharma, P.A.Z. Suarez, J.M. Perez, S.Z. Erhan. Oxidation and low temperature properties of biofuels obtained from pyrolysis and alcoholysis of soybean oil and their blends with petroleum diesel. Fuel Processing Technology 2009; 90(10): 1265- 1271.

[76] S.V. Arau´ jo, F.M.T. Luna, E.M. Rola Jr, D.C.S. Azevedo, C.L. Cavalcante Jr. A rapid method for evaluation of the oxidation stability of castor oil FAME: influence of antioxidant type and concentration. Fuel Processing Technology 2009; 90(10): 1272- 1277.

[77] M. Mittelbach, S. Schober. The influence of antioxidants on the oxidation stability of biodiesel. Journal of the American Oil Chemists Society 2003; 80: 817–23.

[78] S. Schober, M. Mittelbach. The impact of antioxidants on biodiesel oxidation stability. European Journal of Lipid Science & Technology 2004; 106: 382–9.